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聚芴类刚柔嵌段共聚物的制备及其性能研究

Synthesis of Polyfluorene-based Rod-coil Block Copolymers and Studies on their Properties

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摘 要

聚芴类刚柔嵌段共聚物近年来由于其在光电材料上的广泛应用而备受瞩目。柔性段的引入不仅能调控聚芴类聚合物的光电特性，更能提高对其形貌的灵活控制。然而，分子结构以及相形态对聚芴类聚合物光电性质的影响研究的还不够完善，并且聚芴类蓝光材料的长波发射问题亦急需解决。因此，本论文设计并合成了含有不同柔性段结构的聚芴类刚柔嵌段共聚物来探讨分子结构及相形态对其光电性质的影响，同时也对其薄膜状态下的表面性质及光谱稳定性进行了研究。主要内容如下：

1. 结合 Suzuki 反应以及原子转移自由基聚合（ATRP）技术制备了聚芴与氟化丙烯酸酯的刚柔嵌段共聚物聚[2,7-(9,9-二己基芴)]-b-聚甲基丙烯酸七氟丁酯（PF-b-PHFBMA），通过核磁共振（NMR）、傅里叶红外光谱（FT-IR）和凝胶渗透色谱（GPC）对其结构进行了表征，然后通过透射电镜（TEM）及动态光散射（DLS）对其在溶液中的自组装行为进行了考察，接着通过紫外吸收光谱（UV-abs）及荧光发射光谱（PL）对其在溶液中的光谱行为进行了研究，最后通过静态水接触角（WCA）及扫描电镜（SEM）等手段对其表面性质进行了了探讨。TEM 和 DLS 的结果表明，随着 PHFBMA 嵌段长度的增加，聚合物在 THF 中的胶束形貌由球状逐渐变成棒状，并且胶束的粒径经历了先增大后减小的变化；UV-abs 和 PL 光谱的结果表明，聚合物的光物理性质并不依赖于 PHFBMA 嵌段的引入及 PHFBMA 嵌段长度的改变；表面性质的结果表明，PHFBMA 嵌段的引入能够很好的提高聚合物的表面疏水性以及降低聚合物的表面能，并且不同的溶液胶束结构对聚合物薄膜的表面含氟量有着明显的影响，同时，在微相分离及聚集的作用下，也得到了具有多样化形貌的聚合物薄膜，这在聚芴类光电器件的运用上有着潜在的价值。

2. 采用 ATRP 的技术合成了含不同柔性段的聚芴刚柔嵌段共聚物聚[2,7-(9,9-二己基芴)]-b-聚甲基丙烯酸正丁酯（PF-b-PBMA），聚[2,7-(9,9-二己基芴)]-b-聚甲基丙烯酸羟乙酯（PF-b-PHEMA）和聚[2,7-(9,9-二己基芴)]-b-聚丙烯酸（PF-b-PAA），并通过核磁共振（NMR）、傅里叶红外光谱（FT-IR）和凝胶渗

透色谱（GPC）对其结构进行了表征，然后考察了不同柔性段对聚芴类刚柔嵌段共聚物在单溶剂中的自组装行为，同时也考察了不同类型选择性溶剂（THF、$CHCl_3$ 和 $C_2Cl_3F_3$）对其自组装行为的影响。接着，通过 UV-abs 以及 PL 光谱考察了不同柔性段在单选择性溶剂中自组装行为对其光谱行为的影响。最后采用这些自组装溶液进行滴铸成膜，考察了自组装行为对其表面性质的影响。自组装行为研究的结果表明，在 THF 中，聚合物趋于形成杆状和球状结构，而不同选择性溶剂对刚性段和柔性段选择性的不同使得聚合物形成了不同的自组装形貌。UV-abs 以及 PL 光谱的结果表明，聚芴刚柔嵌段共聚物若形成以 PF 嵌段为壳、以柔性段为核的自组装结构，则对其光物理性质影响不大，而若形成以 PF 嵌段为核、以柔性段为壳的自组装结构，则会使其 UV-abs 和 PL 光谱发生蓝移。表面性质的结果表明，在柔性段的亲疏水性影响聚合物整体的亲疏水性的同时，不同的自组装结构同样对聚合物的亲疏水性有着影响。

3. 在以上工作的基础上，我们通过紫外吸收光谱（UV-abs）、荧光发射光谱（PL）等手段对含不同柔性段的刚柔嵌段共聚物薄膜在不同热处理情况下的光谱稳定性进行了研究。我们发现，PHFBMA 嵌段的引入会促使聚合物长波发射的产生，而 PBMA、PHEMA 和 PAA 嵌段的引入则有抑制聚合物长波发射的作用，我们认为这是因为柔性段的热运动程度不同造成的。随后，我们对比了热处理前后聚合物薄膜的静态水接触角，发现 PF-b-PHFBMA 薄膜在热处理后静态水接触角明显提升，而 PF-b-PBMA、PF-b-PHEMA 和 PF-b-PAA 薄膜的静态水接触角略有下降，这个结果很好的吻合了光谱稳定性中的结论。

关键词：聚芴；刚柔嵌段共聚物；自组装；光物理性质；光谱稳定性；

Abstract

Polyfluorene based rod-coil block copolymers have been widely studied recently due to their potential applications on optoelectronic devices. The incorporation of coil block to polyfluorene could not only manipulate the electron and optoelectronic properties but also provide the flexibility on morphology control. However, the effects of molecular architecture and phase behaviors on photophysical properties of such polymers have not been fully explored, and the long-wavelength emission of polyfluorene-based blue light-emitting diodes also need to be resolved. Therefore, in this thesis, polyfluorene-based copolymers with different coil blocks were well designed and synthesized in order to explore the effects of molecular architecture and morphology on photophysical properties, and the effects on the surface properties were also studied. The main content is summarized as follows:

1. Poly[2,7-(9,9-dihexxylfluorene)]-b-poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate) (PF-b-PHFBMA) was successfully synthesized by using Suzuki reaction and atom transfer radical polymerization (ATRP) method. The chemical structure was confirmed by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and infrared spectroscopy (FT-IR), and the molecular weight and the weight distribution was charactered by gel permeation chromatography (GPC). Then, transmission electron microscopy (TEM) and dynamic light scattering (DLS) was introduced to study the self-assembly behavior in dilute solution, UV-vis absorption (UV-abs) and photoluminescence (PL) spectra were used to explore the photophysical properties, and static water contact angle (WCA), XPS and SEM were used to study the surface properties. The result of TEM and DLS showed that the micelle's morphology of PF-b-PHFBMA in THF changed from spherical structures to rod-like structures as the increasing of the length of PHFBMA segment, and the diameter of particles increased firstly and then decreased. The result of UV-abs and PL spectral indicated that the photoshysical properties of PF-b-PHFBMA in THF did not depend

on the incorporation of PHFBMA segment or the variation of the length of PHFBMA block. The result of surface properties indicated that the introduction of PHFBMA segment into polyfluorene indeed improved the surface hydrophobicity, and the different structures of micelles had significant influence on the fluorine content of the surface. Finally, we also found that the incorporation of PHFBMA to polyfluorene could form diversified surface morphology, which led to potential application in light-emitting devices.

2. Poly[2,7-(9,9-dihexxylfluorene)]-b-poly(butyl methacrylate) (PF-b-PBMA), Poly[2,7-(9,9-dihexxylfluorene)]-b-poly(2-hydroxyethyl methacrylate) (PF-b-PHEMA) and Poly[2,7-(9,9-dihexxylfluorene)]-b-poly(acrylic acid) (PF-b-PAA) were successfully synthesized by ATRP method. ^{1}H NMR, FT-IR and GPC were used to charactered their chemical structure and molecular weight. Firstly, the self-assembly behavior of these polymers in THF was explored, and the influence of different kind of selective solvent on the self-assembly behavior had also been studied. Then, the effect of the self-assembly behavior on the photophysical properties was investigated by UV-abs and PL spectra. Finally, the influence of the self-assembly behavior on the surface properties had been studied, too. The result of self-assembly behavior showed that polyfluorene-based copolymers with different coil segments trended to form spherical and rod-like micelle and different selective of polyfluorene-based rod-coil copolymers resulted in different micelle's morphology. The result of UV-abs and PL spectra indicated that the formation of micelles composed of a PF corona and a PHFBMA core did not exhibit noticeable influence on the optical properties, however, the formation of micelles composed of a PF core and a PHFBMA corona resulted in a blue shift in both the absorption spectra and the fluorescence spectra due to the H-aggregation of the PF block. The result of surface characteration showed that both the coil block and the structure of micelles had influence on the surface properties.

3. Based on the above work, the spectral stability of polyfluorene-based rod-coil copolymers was investigated. The result showed that the incorporation of PBMA, PHEMA and PAA segments to polyfluorene indeed improved the spectral stability,

while the incorporation of PHFBMA block promoted the long-wavelength emission. We owed it to the influence of different degree of molecular movement when heated. Besides, we compared the water contact angle (WCA) of the films before and after heated, and found that the WCA of the film of PF-b-PHFBMA increased obviously, while the WCA of the films of PF-b-PBMA, PF-b-PHEMA and PF-b-PAA decreased slightly, these were well anastomotic to the results of the spectral stability.

Keywords: Polyfluorene; Rod-coil Copolymer; Self-assembly; Photophysical Properties; Spectral Stability

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前 言

近年来，刚柔嵌段共轭聚合物因其独特的性质而引起了人们广泛的关注。一方面刚柔嵌段聚合物能够自组装形成方便可调的一维、二维以及三维的周期性微结构；另一方面，共轭刚性段的存在使得聚合物具有刚性段的性质，例如无机半导体特性和金属导电性等，因而在光电转换、聚合物太阳能电池、生物传感器等领域有着广泛的应用。

在众多的共轭聚合物中，聚芴作为一种重要的蓝光材料，因其优异的薄膜荧光量子效率和热稳定性而得到人们的深入研究。然而，对于聚芴类聚合物的结构与光物理性质的关系研究的还不够完善，仍需要不断的深入考察。此外，聚芴在加热或者器件运行过程中容易产生长波射，严重影响器件发光的饱和色纯度、效率和稳定性。近年来，人们开始尝试引入共轭或非共轭的非规整结构单元到聚合物中，利用空间位阻和构象来抑制链间刚性结构的聚集进而控制红光发射。其中，刚柔嵌段结构亦被提出，一方面刚柔嵌段结构在能很好的保持刚性段光电性质的同时也将柔性段的性质结合到了聚合物中，另一方面嵌段之间的微相分离行为能够使聚合物形成一系列的超分子纳米结构，因而可通过这种多样化的空间结构来减弱聚芴刚性段分子间的聚集，同时亦可通过功能化柔性段的引入给聚合物带来新的性质。

基于以上认识，本文制备了含有不同柔性段结构的聚芴类刚柔嵌段共聚物，并对它们在溶液中的相形态及光物理性质进行了探讨，同时也对其薄膜的表面性质与热处理下的光谱稳定性进行了考察。